Development of New Fullerene Functionalization

著者	SI Weili
学位授与機関	Tohoku University
学位授与番号	11301甲第16190号
URL	http://hdl.handle.net/10097/60403

博士論文

Development of New Fullerene Functionalization

(新規フラーレン官能基化反応の開発)

Weili Si

平成２６年

Contents

Abstract

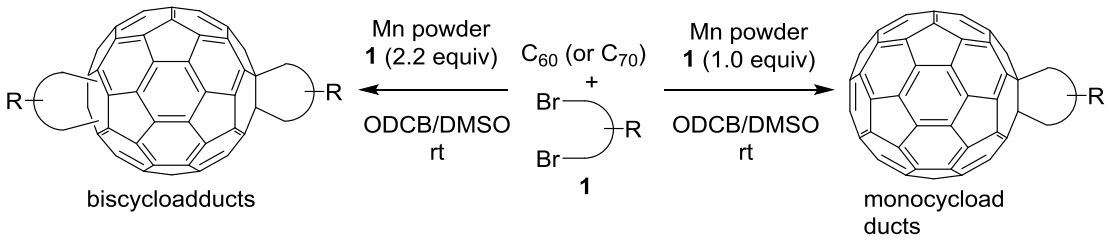
Introduction

Functional fullerenes have been used broadly as excellent n-type semiconductors in solution processable organic electronics, especially as the unique electron acceptors for organic photovoltaics (OPVs) due to their significant increase in solubility while preserving certain electronic and optical properties of pristine fullerenes. To achieve low-cost OPVs, synthesis of OPV materials in a simple, practical process with a high production yield is one of the important strategies. Numerous efforts have been made to develop new fullerene functionalization. In comparison with the traditional methods, such as nucleophilic addition of organometallic reagents, cycloaddition, and addition of free radicals, the transition-metal-promoted fullerene functionalization has been proved to exhibit high efficiency and selectivity under mild reaction conditions as well as a high compatibility with a wide range of functional groups. In this context, I have developed novel Mn-mediated highly efficient fullerene cycloaddition, Cu-catalyzed selective C-H monoamination of hydrofullerenes, and NBS-promoted oxidation of a fullerene monoradical for selective synthesis of 1,4-bisaddcuts.

Results and Discussion

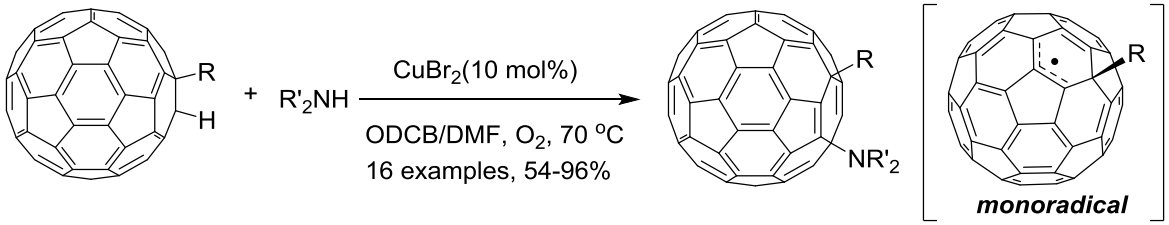
1. Mn Powder-Promoted Highly Efficient Fullerene Carbocycloaddition at Room Temperature[1]

Discovery of an efficient, practical, and flexible synthetic method to produce various important electron acceptors for low-cost organic photovoltaics is highly desirable. Although the most commonly used acceptor materials, such as $PC_{61}BM$, $PC_{71}BM$, $IC_{60}BA$, bis$PC_{61}BM$ are commercially available, they are still very expensive mainly due to their low production yields and limited synthetic methods. I have developed an unprecedented, highly efficient, and practical Mn powder-promoted fullerene carbocyclization for the synthesis of various mono- and biscycloadducts in good to high yields. Notably, the standard OPV acceptors, PCBMs, have been obtained in higher than 95% yields, which cannot be achieved under the previously reported methods.



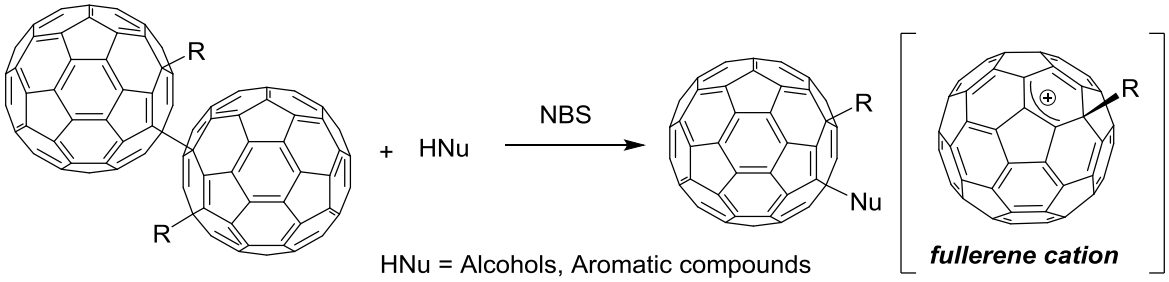
2. Cu-Catalyzed C-H Amination of Hydrofullerenes Leading to 1,4-Difunctionalized Fullerenes[2]

A novel and highly efficient Cu-catalyzed C-H amination of the monofunctionalized hydrofullerenes for the synthesis of 1,4-difunctional fullerenes has been reported. A new series of 1,4-fullerene derivatives having various monoamine addends were synthesized in good to high yields under mild reaction conditions. The experimental results indicated that the present reaction proceeds through the formation of a fullerene monoradical by an amine followed by coupling with an amine radical generated by a $CuBr_2$ catalyst under an oxygen atmosphere.



3. NBS-Promoted Oxidation of Fullerene Monoradicals Leading to Regioselective 1,4-Difunctional Fullerenes[3]

Fullerene monoradical has become a useful intermediate for the selective functionalization of fullerenes, which exhibits versatile activity for the synthesis of various novel functional fullerenes through the oxidation to a fullerene cation or direct coupling with other radicals, while its potential reactivity is still less explored. I have demonstrated that NBS is able to promote the oxidation of fullerene monoradicals to form 1,4-difunctional fullerenes. The singly bonded fullerene dimers were used as fullerene monoradical precursors, which produced various 1,4-fullerenes with a wide range of functional groups in good to high yields with high regioselectivity in terms of cosolvents and nucleophiles.



1. Si, W.; Zhang, X.; Lu, S.; Yasuda, Y.; Asao, N.; Han, L.; Yamamoto, Y.; Jin, T. **2014**, *submitted*.
2. Si, W.; Lu, S.; Bao, M.; Asao, N.; Yamamoto, Y.; Jin, T. *Org. Lett.* **2014**, *16*, 620–623.
3. Si, W.; Lu, S.; Bao, M.; Asao, N.; Yamamoto, Y.; Jin, T. *Chem. Commun.* **2014**, *50*, 15730–15732.